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Near-IR spectrum of polybutadiene

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Abstract

The vibrational overtone spectrum of polybutadiene was recorded up to $14,000\text{ cm}^{-1}$ and interpreted in the local mode model. The methylenic and olefinic CH stretch progressions, with anharmonicities of 66 and 59 cm^{-1} , respectively, were identified for $\Delta v = 2, 3, 4$ and 5 . The vinyl stretch progression, being much weaker, was identified through the $\Delta v = 3$ transition. Several bending progressions appeared belonging to the *cis*, *trans* and vinyl isomers, two of which belong specifically to the vinyl bending motion. The anharmonicities for these bends vary from 11 to 15 cm^{-1} . The relative intensity of stretching features decreased on average by a factor of 8 with each higher quantum transition while the comparable decrease for the bending absorptions was a factor of 4 .

Introduction

The optical determination of the microstructure in polybutadiene and butadiene-styrene copolymers originated in the low energy infrared spectrum where characteristic absorptions for the *trans*, *cis* and vinyl conformers were identified¹. Bands at 10.34 , 10.98 and 14.7 microns were used to identify the *trans*, *cis* and vinyl polymers, respectively. The quantitation of the relative amounts of conformers used a spectroscopic method assuming the additivity of absorptivity¹ where the molar absorptivities for *trans*, *cis* and vinyl octenes were assumed to represent those of the butadiene isomers.

Absorption features in the near-IR belonging to the vinyl CH stretch (1.636 microns) and the methylenic CH stretch (1.762 microns) were used in conjunction with NMR measurements to develop a quantitative determination of the microstructure of butadiene from sodium, butyllithium and free-radical catalyzed polybutadienes.² The molar absorptivity did vary linearly with the number average molecular weight of the samples with the slope depending on the type of polymerization used. In addition the number of groups (methylenic or vinyl) as determined by NMR varied linearly with the molar absorptivity for various samples. Thus the intensity of the individual near-IR absorptions can be used to determine the microstructure of the polybutadienes.

An improved method for the optical determination of the polybutadiene microstructure applied classical least squares (CLS) and principal components regression to estimate the spectrum of pure *cis*, *trans* and vinyl polymer in polybutadiene samples.³ These estimated spectra for the pure isomers covered the region from 3000 to 9100 cm^{-1} . Although spectroscopic assignments of individual peaks were not complete the overall procedure determined the % mass of the *cis*, *trans* and vinyl isomers.

In this report the vibrational overtone spectrum of polybutadiene is discussed in terms of local mode theory^{4, 5} which has been developed for the visible vibrational spectra of gaseous and liquid molecular samples. For molecular samples above 7000 cm^{-1} the most intense peaks belong to progressions which can be assigned to CH, NH or OH bond stretches. Furthermore the various structurally nonequivalent CH bonds contribute their own progression to the spectrum. Progressions for in-plane and out-of-plane methyl^{6, 7}, methylenic, olefinic⁸, acetylenic, vinylic and even equatorial and axial CH⁹ types have been distinguished from one another. Fitting the transition energies for a single progression to a Birge Spomer plot yields the anharmonicity and mechanical frequency for that local bond oscillator⁴. Because of this anharmonicity peaks from the various nonequivalent oscillators are further and further separated from one another at each higher overtone. Thus at the fourth CH overtone the methylenic peak may be separated by as much as 500 cm^{-1} from the olefinic peak. Even with the typical peak broadening these two can be easily assigned.

High vibrational overtone spectra of polymers have been recorded. Manzanares¹⁰ assigned the $\Delta v = 3$ and 4 CH stretch transitions of *cis*-1,4-polybutadiene in CCl_4 by comparison to the overtone spectra of liquid *cis* and *trans*-hexene. The olefinic transitions were within 7 cm^{-1} of those observed in hexene. The methylenic peak appeared to have a low energy shoulder at each quantum level which was assigned as the pseudoequatorial CH stretch. This proposed assignment reflected the assignments from liquid *cis*-3-hexene and cycloalkenes. The overtone spectrum of polyethylene film¹¹ clearly displays the CH bond stretches through the fourth overtone ($\Delta v = 5$) with an anharmonicity of 57 cm^{-1} . The bending vibrational overtones are strong and clearly observed through the eighth overtone ($\Delta v = 9$) with an anharmonicity of 7 cm^{-1} . In molecular samples the bending overtones are weak and often only observed when they interact through vibrational coupling with the stretching motion.¹²

With respect to polybutadiene Figure 1 clarifies the types of nonequivalent CH bonds which are expected to give rise to separate local mode absorptions in the near-IR spectrum. In *trans*-polybutadiene each repeating unit has four methylenic and two olefinic CH bonds. The methylenic CH bonds are further distinguished from one another from their positions as equatorial or axial¹⁰ with respect to the double bond. The *cis*-polybutadiene has the same

number of methylenic and olefinic CH bonds but both olefinic CH bonds are *cis* as opposed to *trans* to one another. Vinyl polybutadiene possesses one olefinic, two methylenic and one tertiary CH bonds. In addition all the conformers terminate with methyl groups but these methyl CH bonds are expected to be at such low concentration as to not be observed.

Experimental

The spectra were recorded on a Mattson FT near-IR spectrometer with a tungsten lamp and quartz beam splitter. A PdSe detector recorded the spectra in the 3000 to 9000 cm^{-1} region and a silicon detector was used from 9000 to 14500 cm^{-1} . Most spectra are the result of 800 scans; however, at the higher energies as many as 1000 scans were used to achieve the desired signal to noise ratio. For the 3000 to 9000 cm^{-1} region, polybutadiene was dissolved in CCl_4 . The concentrations ranged from 6 mg/ml for the 2000 to 3500 cm^{-1} range, 80 mg/ml for the 3500 to 6500 cm^{-1} range, to 890 mg/ml (pure liquid) for the 6500 to 14000 cm^{-1} range. The spectra in the mid-IR were obtained on a Mattson FTIR with a globar source, KBr beamsplitter and MCD detector. All spectra were recorded at 1 cm^{-1} resolution.

Results and Discussion

The vibrational spectrum of polybutadiene is shown in Figure 2. The absorbance scale on this spectrum belongs to the lowest trace. Portions of the spectrum have been expanded so the weak bands at high energy can be discerned. The concentrations used for recording each spectral range of the spectrum are given in the figure caption.

The transition energies (in cm^{-1}) for a local mode progression a single type of nonequivalent bond fit the following equation⁴

$$\Delta E = (w_e - w_e x_e)v - w_e x_e v^2$$

where w_e is the mechanical frequency, $w_e x_e$ is the anharmonicity and v is the local mode quantum number. A Birge-Sponer plot of $\Delta E/v$ and v produces the anharmonicity and mechanical frequency for that local mode.

The CH stretch progressions for the olefinic and methylenic bonds in the *cis* and *trans* isomers are easily identified based on previous work.^{2, 3, 10} Fitting the $\Delta v = 2$ through $\Delta v = 5$ transition to a Birge-Sponer plot yields anharmonicities of 66 and 59 cm^{-1} for the methylenic and olefinic stretches, respectively. From the CLS estimated spectra it appears that the *trans* and *cis* olefinic CH stretch transitions should be overlapped, broadening the peaks in the *cis-trans* mixture relative to the pure isomer. However, this is not the case as seen from a direct comparison of the second overtone of the CH stretch in our polybutadiene spectrum and Manzanares' pure *cis* isomer in Figure 3. No difference in the positions and widths of the

olefinic peaks can be observed. In addition no separation of the axial and equatorial CH stretches is evident in our mixed polybutadiene spectrum. This fact probably accounts for the difference in the relative intensities of the olefinic and methylenic peaks in the two spectra. In *cis*-1,4-butadiene the methylenic peak was weaker than the olefinic whereas in this work the opposite is true. The vinyl CH stretch occurs at higher frequency than the methylenic and olefinic stretches and possesses a much higher anharmonicity of 73 cm^{-1} . This anharmonicity may be an over estimate since only two members of the progression were used in the calculation.

The bending region of the spectrum is easily identified when the change in the bend quantum number is odd ($\Delta v = \text{odd}$). Since the CH bend frequency is about half that of the CH stretch frequency the Δv even transitions lie to the blue side of the CH stretch band contour. A pair of prominent peaks of approximately equal intensity each form a progression with anharmonicities of 10 and 17 cm^{-1} , for the lower and higher frequency progressions, respectively. These are the CH bending progressions. These progressions may belong to the methylenic and olefinic CH bond bends in the *cis* and *trans* isomers.

In the bending region the peaks at 4717 and 4484 cm^{-1} were identified as belonging to the vinyl isomer in the CLS estimated spectra.³ The 4717 peak fits in a Birge-Sponer plot with the peak at 7750 cm^{-1} yielding an anharmonicity of 11 cm^{-1} . The 4481 cm^{-1} peak fits with an anharmonicity of 13 cm^{-1} with the peak at 7346 cm^{-1} . These two progressions arise from the symmetric and antisymmetric bends of the vinyl CH bonds. The final bending progression of which two members can be identified, the 4597 and the 7508 cm^{-1} peaks, has an anharmonicity of 15 cm^{-1} . The peak at 4597 cm^{-1} appears in the spectra of all three isomers in the CLS estimated spectra.³

The relative integrated intensities of the absorption features (tabulated in Table 2) were estimated by integrating the area under an absorption and scaling this value by the concentration. The integrations from several spectra, taken at different analyte concentrations, were averaged to provide a more accurate intensity. Most of the peaks are overlapped which limits the reliability of the intensity measurements. In these integrations the entire CH stretch peak area was integrated with no attempt to separate the olefinic and methylenic CH oscillators. Table 2 provides the wavelength ranges selected for integration of each overtone. The integrations for these CH oscillators include the entire major peak area, but exclude some small peaks to each side. Although these small peaks are clearly observed at low energies, at higher overtones they are even weaker and should not be included in the integration. The relative intensities, scaled to the first overtone area (100%) in the case of the CH stretch and to the second overtone in the case of the CH bend, are tabulated in Table 2.

The intensity of the second CH stretch overtone was found to decrease by a factor of 6 from that of the first overtone. Similarly the third overtone was a factor of 10 weaker than the second overtone and the fourth was a factor of 8 weaker than the third. Similar factors for gaseous molecular samples vary from 8 to 12.^{9, 13} These integrating operations were performed on the CH bends as well, and the drop-off factor was found to be 5 for each quantum level from $v=3$ to $v=5$, while 3 was the factor of decreasing peak intensity for the quantum levels from $v=5$ to $v=7$.

Conclusions

The local mode assignments of the vibrational overtone spectrum of polybutadiene have been made for the $\Delta v = 2, 3, 4$ and 5 CH stretch transitions and the CH bend transitions for $\Delta v = 3, 5$ and 7. The Δv even transitions for the bending motion fall together with the CH stretching transitions and was therefore difficult to observe. The methylenic and olefinic CH stretches were distinguished at each quantum level transition. The vinyl CH stretch transitions occurred at frequencies higher than those of the methylenic and olefinic but being weaker was only observed for the $\Delta v = 2$ and 3. The anharmonicities for the methylenic and olefinic stretches were 59 and 66 cm^{-1} , respectively, and ranged from 10 to 17 cm^{-1} for the bends. The relative intensities for each successive transition was estimated by integrating the area under the methylenic and olefinic CH stretch band contours. The stretches decrease by a factor of about 8 for each overtone and the bends decrease by a factor of 4. The bending transitions remain intense at high vibrational transitions even though the anharmonicity are relatively small.

Table 1 Transition Wavenumbers, Assignments, Relative Integrated Intensities and Concentrations of vibrational absorptions in 1,4-butadiene

| Transition | Assignment | Previous Work |
|------------|---------------------------------|--|
| 4243 | $\nu=3$ <i>cis-trans</i> bend 1 | |
| 4330 | $\nu=3$ <i>cis-trans</i> bend 2 | 4318 ^b |
| 4481 | $\nu=3$ vinyl bend | 4484 vinyl combination ^b |
| 4597 | $\nu=3$ bend | |
| 4660 | | |
| 4717 | $\nu=3$ CH vinyl bend | 4719 combination ^a , 4721 vinyl combination ^b |
| 5657 | $\nu=2$ methylenic stretch | 5675 methylenic stretch ^a |
| 5823 | $\nu=2$ olefinic stretch | 5821 methylenic comb ^a |
| 6008 | | 5889 methyl ^a |
| 6110 | $\nu=2$ vinyl stretch | 6112 vinyl stretch ^b |
| 6367 | | |
| 6453 | | |
| 7051 | $\nu=5$ <i>cis-trans</i> bend 1 | |
| 7173 | $\nu=5$ <i>cis-trans</i> bend 2 | |
| 7346 | | |
| 7508 | $\nu=5$ bend | |
| 7750 | $\nu=5$ vinyl bend | |
| 8286 | $\nu=3$ methylenic stretch | 8278, 8408 ax,eq methylenic stretch ^c |
| 8552 | $\nu=3$ olefinic stretch | 8583 olefinic stretch ^c |
| 8934 | | |
| 8947 | $\nu=3$ vinyl stretch | |
| 9032 | | |
| 9620 | $\nu=7$ vinyl bend | |
| 10143 | | |
| 10801 | $\nu=4$ methylenic stretch | 10773, 10936 ax, eq methylenic stretch ^c |
| 11163 | $\nu=4$ olefinic stretch | 11199 olefinic stretch ^c |
| 13140 | $\nu=5$ methylenic stretch | |
| 13669 | $\nu=5$ olefinic stretch | |

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c. Carlos Manzanares, I, Victor M. Blunt and Jingping Peng, Spectrochimia Acta. 49A(8), 1139 (1993).

Table 2 Wavelength Ranges for Integrations

| Overtone | Integration Range (cm ⁻¹) | | Relative Intensity (%) |
|--------------|---------------------------------------|-------|------------------------|
| CH Stretch | | | |
| $\Delta v=2$ | 5270 to | 6170 | 100 |
| $\Delta v=3$ | 7920 to | 9030 | 17 |
| $\Delta v=4$ | 10330 to | 11510 | 1.7 |
| $\Delta v=5$ | 12650 to | 14210 | 0.0022 |
| CH Bend | | | |
| $\Delta v=3$ | 3970 to | 4430 | 100 |
| $\Delta v=5$ | 6860 to | 7380 | 4.0 |
| $\Delta v=7$ | 9190 to | 10130 | 0.44 |

Table 3 Mechanical frequencies and anharmonicities in wavenumbers (cm^{-1})

| | Mechanical frequency | Anharmonicity |
|-------------------------|----------------------|---------------|
| methylenic CH stretch | 3028 ± 8 | 66 ± 1.4 |
| olefinic CH stretch | 3088 ± 3 | 59 ± 0.6 |
| <i>cis-trans</i> bend 1 | 1460 ± 24 | 10 ± 4.6 |
| <i>cis-trans</i> bend 2 | 1521 ± 40 | 17 ± 7.4 |
| vinyl bend 1 | 1556 | 11 |
| vinyl bend 2 | 1469 | 14 |

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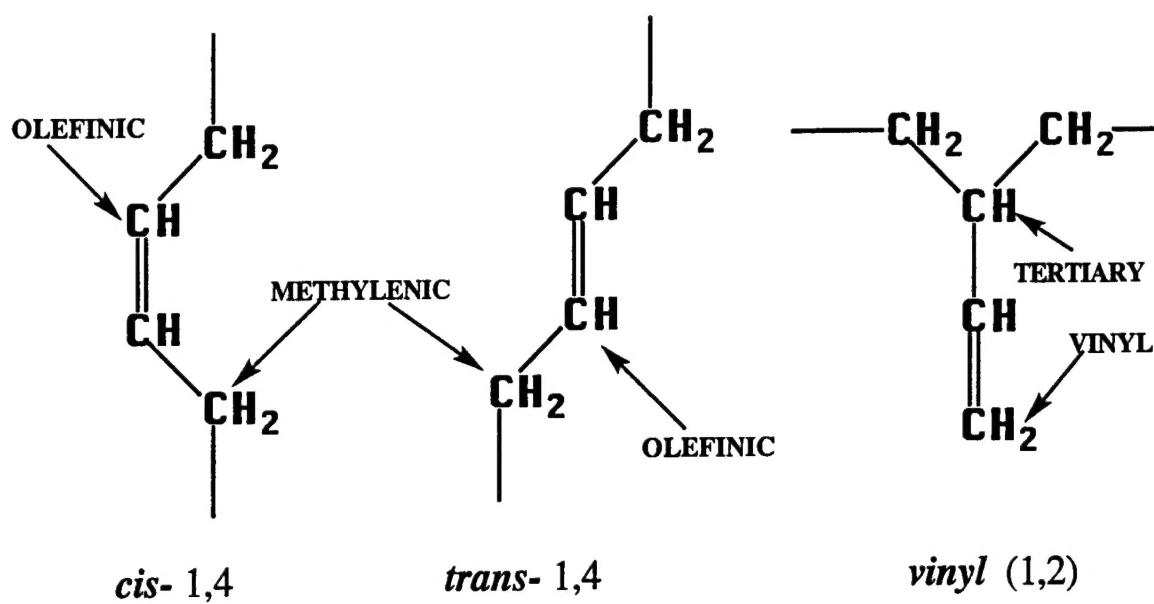
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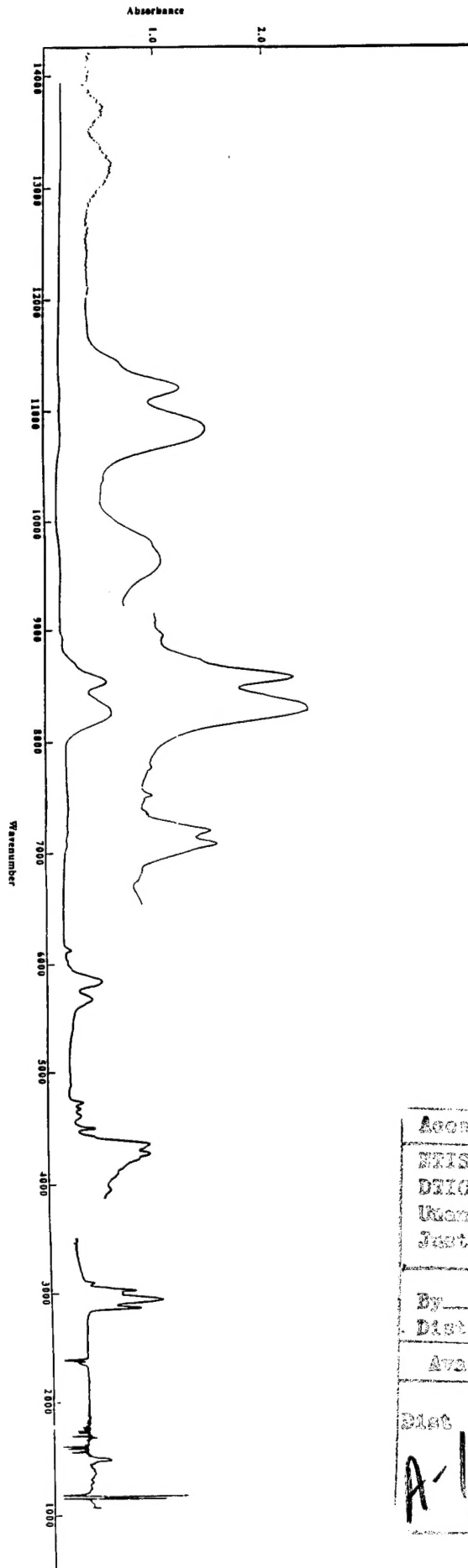
Figure Captions

Figure 1 Isomers of 1,4-butadiene and the nonequivalent types of CH bonds

Figure 2 Vibrational spectrum of polybutadiene. The concentrations of the samples were: 6 mg/ml for the 2000 to 3500 cm^{-1} range; 80 mg/ml for the 3500 to 6500 cm^{-1} range; 890 mg/ml (pure liquid) for the 6500 to 14000 cm^{-1} range

Figure 3 Comparison of the spectrum of polybutadiene (straight line) with *cis*-1,4-polybutadiene (hatched line - reference 10)





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